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Deposited in DRO:

06 September 2021

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Rowbotham, Jack and Greenwell, Chris and Dyer, Philip W. (2021) 'Opening the Egg Box: NMR spectroscopic analysis of the interactions between s-block cations and kelp monosaccharides.', Dalton Transactions, 50 (38). pp. 13246-13255.

Further information on publisher's website:

https://doi.org/10.1039/D0DT04375C

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Electronic Supplementary Information (ESI)

Opening the *Egg Box*: NMR spectroscopic analysis of the interactions between s-block cations and kelp monosaccharides

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1 Contents

2 Materials and methods

2.1 Reagents and solutions

All chemicals were purchased from Sigma-Aldrich, with the exception of D_2O (99.8 %) from Apollo Scientific, and used as received unless otherwise stated. Norell® XR-55-7 NMR tubes (5.0 mm) were used throughout.

Sodium salts of L-guluronate (**GulA**) and D-mannuronate (**ManA**) were prepared from alginate obtained from *Laminaria digitata*, according to the methods described previously.[1] Sodium salts of D-glucuronate (**GlcA**) and -D-galacturonate (**GalA**) were obtained from commercial vendors (Sigma-Aldrich). All non-uronates were exchanged with D_2O and adjusted to the correct concentration using previously described procedures.[1]

D_2O solutions of NaCl, KCl, $CaCl_2$, $Ca(NO_3)_2$, $SrCl_2$, $BaCl_2$ (1.2 M) were made up by dissolving the appropriate mass of the hydrated metal salt in D_2O, evaporating at 150 °C for 3 hours, and then re-dissolving the anhydrous salt in the required volume of fresh D_2O. A solution of $MgCl_2$ in D_2O (1.2 M) was made by dissolving the anhydrous metal salt directly into the required volume of liquid and then re-adjusting the pD to 7.9 with small additions of DCl. A solution of CaI_2 in D_2O was made by dissolving the anhydrous metal salt directly into the required volume of liquid under an inert N_2 atmosphere, with no further adjustments.

The pD of solutions was measured using a Sigma-Aldrich micro pH combination electrode (glass body, 183 mm L, 3.5 mm OD) connected to an Orion Star™ A111 pH-meter, calibrated with standard H_2O buffers. The pD was then calculated by adding 0.4 units to the reading of the meter. Whilst the pD of metal-free solutions can be determined quite accurately, those with extremely high ionic strengths can cause difficulties.[2,3] Hence, whilst the pD values of the blank (metal-free) solutions were measured directly from the meter, the pD of metal-rich solutions were double-checked with Fisherbrand™ pH-Fix Test Strips. In addition, preliminary experiments indicated that, for studies conducted at pD 7.9, small variations of the pD (between pD 6.4 to 9.4) had no measurable effects with regards to the relative chemical shifts and peak ratios.

2.2 ^{1}H and ^{13}C NMR spectroscopy – experimental parameters

^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance NMR spectrometer according to the parameters described in Table S.1. A flame-sealed glass capillary (1.0 mm OD) containing $CHCl_3$ in $CDCl_3$ (5:95 vol.%) was inserted co-axially into each solution to provide an external reference signal.[4,5]

Table S.1 NMR spectrometer acquisition parameters

Bruker Avance-400 MHz		
Experiment	**^{1}H**	**^{13}C***
RF frequency (MHz)	400.13	100.62
Temperature (K)	295 ± 2	295 ± 2
Number of scans	8	1024
Pulse width (μs)	10.0	8.00
Spectral width (Hz)	8000	24000
Acquisition time (s)	4.09	1.36
Relaxation delay (s)	1.00	2.00

*proton decoupled

Metal/uronate screening: D_2O solutions of sodium uronate (100 μL, 260 mM, pD 7.9) were combined with those of a chosen metal salt (500 μL, 1.2 M, pD 7.9) and shaken together to yield the analyte solution (600 μL, 1.0 M metal, 43 mM uronate, pD 7.9). After 12 hours at room temperature, the ^{1}H NMR spectrum was acquired. The pD of the solution was then reduced to 1.4 by the addition of 25 μl of 2.5 M DCl, and the spectrum was re-acquired after 12 hours. Preliminary experiments (and literature examples)[6] indicated that the pyranose anomeric equilibrium settles very quickly after a metal ion has been added (on the order of minutes), with no further changes being detected on standing at pD 7.9 for a number of months. On leaving the solutions to stand for 48 hours at pD 1.4 however, the solutions of **GulA**, **GlcA**, and **ManA** begin to give rise to additional sets of smaller peaks in their ^{1}H NMR spectra. These peaks correspond to the spontaneous lactonisation of the uronates in the acidified conditions.[1] Lactone formation occurs at a much slower rate (days to weeks) than changes to the anomeric equilibria (minutes), and so the effects of metal ions on lactonisation were not considered further.

Calcium/uronate titrations: D_2O solutions of **GulA**, **ManA**, and **GlcA** (500 μL, 260 mM, pD 7.9) were titrated with small amounts of $CaCl_2$ (6.5 M in D_2O) to give [Ca^{2+}] concentrations ranging from 0.00 to 1.30 M. Following each addition, the solution was shaken, and allowed to stand at room temperature for a minimum of 1 hour prior to the acquisition of ^{1}H and ^{13}C NMR spectra. The small changes in the concentration of the solution with the increasing volume were found to be negligible. The experiment could not be performed for **GalA** because addition of $CaCl_2$ led to the formation of a white precipitate after a few hours, preventing suitable NMR spectra from being acquired.

2.3 ^{1}H and ^{13}C NMR spectroscopy – general data processing

Data processing was carried out in MestReNova 10.0.2-15465. Peak integration was performed manually on only clearly defined signals using the "sum" mode in MestreNova to generate the absolute integral without any additional correction. In cases where the centre of a peak was hard to determine in the 1D ^{1}H NMR spectrum due to overlap with neighbouring signals, a suitable cross peak in the ^{1}H-^{1}H COSY spectrum was used to determine the peak centroid position. The ^{1}H and ^{13}C NMR assignments of **GulA** and **ManA** were as reported previously, and those for **GalA** and **GlcA** are given in Tables S.2 and S.3. In addition to the 1D spectral acquisitions, 2D NMR spectroscopic experiments (^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC) were performed at suitable intervals to confirm the identity of peaks following significant changes to the spectra and when interchange between signals had taken place.

Table S.2 ^{1}H NMR spectroscopic assignments of sodium mono-uronate salts in D_2O (0.26 ± 0.02 M) at 400 MHz, pD 7.9, and 295 K (relative to $C\underline{H}Cl_3$ in $CDCl_3$, δ = 7.26 ppm).

δ (ppm) J (Hz)	Na-D-glucopyranuronate		Na-D-galactopyranuronate	
	α	**β**	**α**	**β**
δH1	**5.24, d**	**4.64, d**	**5.27, d**	**4.53, d**
$J_{1,2}$	3.8	8.0	3.5	7.9
δH2	**3.57, dd**	**3.28, m**[b]	**3.78, dd**	**3.46, dd**
$J_{1,2}$	3.8	n.d.	3.8	7.9
$J_{2,3}$	9.8	n.d.	10.4	9.9
δH3	**3.72, m**[c]	**3.51, *pt***[d]	**3.87, dd**	**3.65, dd**
$J_{2,3}$	n.d.	n.d	10.1	10.0
$J_{3,4}$	n.d.	n.d	3.5	3.5
δH4	**3.49, m**[d]	**3.51, m**[d]	**4.24, dd**	**4.17, dd**
$J_{3,4}$	n.d.	n.d.	3.6	3.5
$J_{4,5}$	n.d.	n.d.	1.5	1.2
δH5	**4.08, d**	**3.73, m**[c]	**4.37, d**	**4.02, d**
$J_{4,5}$	10.1	n.d.	1.3	1.4

Key: d = doublet, dd = doublet of doublets, *pt* = *pseudo*-triplet, m = multiplet, n.d. = not determined

[a] Scalar couplings (J) are quoted with a precision of ± 0.1 Hz.
[b] Complex multiplet due to strong coupling between βH3 and βH4 at pD 7.9. At pD 1.4, βH2 gives dd with $J_{1,2} = J_{2,3} = 9.1$ Hz.
[c] αH3 and βH5 give overlapping signals at pD 7.9. At pD 1.4, βH5 gives d with $J_{4,5} = 9.6$ Hz, and αH3 gives *pt* with $J_{2,3} = J_{3,4} = 9.6$ Hz.
[d] βH3, βH4, and αH4 overlap considerably, and cannot be resolved at pD 7.9. βH3 gives *pt* with $J_{2,3} = J_{3,4} = 9.6$ Hz when pD = 1.4.

Table S.3 ^{13}C{^{1}H} NMR spectral assignments of sodium mono-uronate salts in D_2O (0.26 ± 0.02 M) at 400 MHz, pD 7.9, and 295 ± 2 K (relative to $\underline{C}DCl_3$, δ = 77.16 ppm).

δ (ppm)	Na-D-glucopyranuronate		Na-D-galactopyranuronate	
	α	**β**	**α**	**β**
δC1	92.31	96.07	92.35	96.15
δC2	71.50	74.20	68.19	71.74
δC3	72.77	75.75	69.51	73.05
δC4	72.30	72.04	70.97	70.51
δC5	72.07	76.44	71.54	75.69
δC6	177.13	176.16	176.18	175.32

2.4 ^{1}H and ^{13}C NMR spectroscopy – coordination chemical shifts ($\Delta\delta$)

The experiments conducted in this work were aimed at discerning the site of metal binding to uronate monomers through measuring changes in the chemical shift (*i.e.* coordination chemical shift, $\Delta\delta$) of both their ^{1}H and ^{13}C signals upon the addition of a metal ion. Here, the $\Delta\delta$ value for a particular nucleus (**n**) following the addition of a metal salt to the solution is defined as:

$$\Delta\delta(\mathbf{n}) = \delta(\mathbf{n})_{\text{in the presence of metal salt}} - \delta(\mathbf{n})_{\text{in metal-free solution}}$$

Changes to δ(**n**) arise as the binding cation distorts the electron cloud surrounding **n**. However, the observed coordination chemical shift ($\Delta\delta_{obs}$) of **n** upon the addition of a metal salt is also effected by "bulk effects" such as the electric fields of non-binding anions and cations.[7–9]

To simplify interpretation, $\Delta\delta_{obs}$ for a particular proton (H*X*) can be measured relative to that of another proton on the same molecule (H*Y*). Such a treatment gives rise to the parameter known as $\Delta\delta_{rel}$, defined as:

$$\Delta\delta_{rel} = \Delta\delta_{obs}(\mathrm{H}X) - \Delta\delta_{obs}(\mathrm{H}Y)$$

In this work, the reference proton (H*Y*) was chosen to be H4. The choice of reference proton was based on the observation that in all pyranose anomers of **GulA**, **ManA**, **GlcA**, and **GalA**, H4 usually gave rise to the largest negative $\Delta\delta_{obs}$ values.

On its own, $\Delta\delta_{rel}$ is not a useful parameter with which to analyse the coordination mode of a particular cation to a particular saccharide; for this the original $\Delta\delta_{obs}$ values must be consulted. However, $\Delta\delta_{rel}$ does facilitate rapid screening of interactions between many different metals with many different uronates by application of the following assumption: if the $\Delta\delta_{rel}$ values for all protons on a uronate anomer in the presence of a selected cation are zero (or close to zero) then that the metal ion is not selectively binding to a particular arrangement of hydroxyl oxygens around the saccharide ring.

Hence, the $\Delta\delta_{rel}$ parameter simplifies the "bulk" effects that occur in the NMR spectra upon the inclusion of a metal salt, allowing for interactions of interest to be rapidly discerned from tables of chemical shift data. For completeness, the tabulated forms of both $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ for all protons in all pyranose anomers of **GulA**, **ManA**, **GlcA**, and **GalA** under the different conditions are given in Section 3.3.

2.5 ^{1}H and ^{13}C NMR spectroscopy – changes to isomeric equilibria

In the discussions below, the following abbreviations are used:

%P = the mol% of pyranose species in solution

%F = the mol% of furanose species in solution

%αP = the mol% of α-pyranose species in solution

%βP = the mol% of β-pyranose species in solution

α/β = the ratio of %αP:%βP

%αF = the mol% of α-furanose species in solution

%βF = the mol% of β-furanose species in solution

σ%αP = the error in %αP

σ%βP = the error in %βP

σ%F = the error in %F

Hence, the following relationships are assumed to be true:

%αP + %βP = %P

%αF + %βF = %F

%P + %F = 100 %

Whilst other authors have relied solely on the ratio of anomeric ^{1}H NMR signals to determine the α/β ratio, the spectra acquired in the preparation of this manuscript were sufficiently well resolved to enable utilisation of signals arising from other protons too. Hence, for each well-resolved signal arising from a proton on a particular conformer, a value for the mol% of that conformer in the solution can be obtained. For example, the integral of the signal of H1 of an α-pyranose conformer measured against a standard reference peak ($\int\alpha$P(H1)), could subsequently be translated into a mol% value (%αP(1)) according to Equation (E.1):

$$\%\alpha\mathrm{P}(1) = \frac{\int \alpha\mathrm{P}(\mathrm{H1})}{\left(\frac{\int \alpha\mathrm{P}(\mathrm{H1}) + \int \alpha\mathrm{P}(\mathrm{H2}) + \ldots \int \alpha\mathrm{P}(\mathrm{H}i)}{i}\right) + \left(\frac{\int \beta\mathrm{P}(\mathrm{H1}) + \int \beta\mathrm{P}(\mathrm{H2}) + \ldots \int \beta\mathrm{P}(\mathrm{H}j)}{j}\right) + \int \alpha\mathrm{F}(\mathrm{H}) + \int \beta\mathrm{F}(\mathrm{H})} \mathrm{X}\,100 \qquad \text{[Eq. E.1]}$$

Where $\int\beta$P(H1), $\int\beta$P(H2), and $\int\beta$P(Hj) represent the integral of signals arising from the β-pyranose anomer, and αF(H) and βF(H) represent the integral of single signals arising from the α- and β-furanose anomers.

Integrating other signals from the same *α*-anomer (*∫α*P(H2), *∫α*P(H3), …*∫α*P(H*i*)) in an analogous fashion to *∫α*P(H1), gives a total of *i* repeat measurements for %*α*P (%*α*P(1), (%*α*P(2)…(%*α*P(*i*)). Averaging %*α*P(1)-(*i*) to give a mean value for %*α*P helps to reduce errors from small variations in the peak areas, baseline, spectral distortions, and so on. However, to minimise possible errors in %*α*P arising from minor fluctuations in temperature, pH, concentrations, ionic strength, *etc.* the entire set of experiments were repeated. The repeat run gave rise to a second set of values for %*α*P: one for Run 1 and one for Run 2. The values from both runs were then combined to give an average value of the mol% of *α*-pyranose in that particular sample according to Equation E.2:

$$\%\alpha\mathrm{P} = \frac{\text{Run 1 } [\%\alpha\mathrm{P}(1) + \%\alpha\mathrm{P}(2) + \ldots \%\alpha\mathrm{P}(i)\,] + \text{Run 2 } [\%\alpha\mathrm{P}(1) + \%\alpha\mathrm{P}(2) + \ldots \%\alpha\mathrm{P}(i)\,]}{2i} \qquad \text{[Eq. E.2]}$$

The uncertainty in the value of %*α*P (σ%*α*P) could then be obtained from Equation E.3:

$$\sigma\%\alpha\mathrm{P} = \frac{\%\alpha\mathrm{P}(\text{max value}) - \%\alpha\mathrm{P}(\text{min value})}{2\sqrt{2i}} \qquad \text{[Eq. E.3]}$$

An identical treatment can then be carried out using peaks assigned to the *β*-pyranose anomer, giving rise to a value for %*β*P and associated uncertainty σ%*β*P. The *α*- and *β*- furanose peaks account for a small percentage of the species in solution (< 10 mol%) and so such an extensive treatment as was carried out for the pyranose configurations was not carried out. Instead, only two peaks (one for the *α*- and one for the *β*-furanose anomers) were integrated and summed together in order to give a single value for %F (and σ%F) in each sample.

When %*α*P and %*β*P had been calculated, a value for the %*α*P:%*β*P ratio (referred to as *α*/*β* in the text) can be calculated according to Equation E.4

$$\alpha/\beta = \frac{\%\alpha P}{\%\beta P} \qquad \text{[Eq. E.4]}$$

α/*β* has an associated uncertainty, σ(α/β), calculated according to Equation E.5:

$$\sigma(\alpha/\beta) = \frac{\%\alpha P}{\%\beta P}\sqrt{\left(\frac{\sigma\alpha P\%}{\%\alpha P}\right)^2 + \left(\frac{\sigma\%\beta P}{\%\beta P}\right)^2} \qquad \text{[Eq. E.5]}$$

2.6 Calculating binding constants for Ca^{2+}/mono-uronate complexes

$CaCl_2$ was added to samples of uronate using the titration procedures described in ESI Section 2.2, leading to changes in the corresponding NMR spectra (see exemplar data for L-guluronate in ESI Section 3.5, and fully tabulated raw data in Section 3.6). Plotting the resulting chemical shift data against the calcium concentration ([Ca^{2+}]) gave rise to the data in Figures 4 and 5 presented in the main manuscript. From the ^{13}C NMR spectral data, it is possible to calculate tentative binding constants between the uronate ligand and Ca^{2+} metal by using the open access *Bindfit* modelling software, available from http://supramolecular.org.[10,11]

In the experiments the total concentration of uronate was known (0.26 M), but the exact concentration of the α- and *β*-pyranose anomers present needed to be determined for each uronate, at each different concentration of Ca^{2+}. Hence, to generate the input files for the fitting algorithm, the concentration of each anomer was therefore calculated by using the ratio of peak integrals in the ^1H NMR spectra, as described in Section 2.5 (full data given in Section 3.6). Using this approach, it was possible to accurately determine the specific [Ca^{2+}]/[ligand] ratio for every level of the titration, and therefore binding constants could be calculated for the individual anomers present in the same solution. For the calculations, a 1:1 Ca^{2+}:ligand complex was assumed, giving rise to the binding constant denoted $K_{1,1}$. Good agreement was found between experimental and fitted data for $K_{1,1}$ using the values for carbons C2-C4 for all of the anomers studied. It was found, however, that the data arising from carbons associated with the carboxylate and ring oxygens (C1, C5, C6) often did not fit well with the other carbons, which is consistent with the hypothesis that more than one binding mode is operative for the calcium-uronate systems. Results for $K_{1,1}$ arising from the data from C2-C4 were as follows (with links to the *Bindfit* calculations):

***$K_{1,1}$*(Ca^{2+}/α-GlcA):** 0.38 M^{-1}; *Error: ± 1.15 %*
http://app.supramolecular.org/bindfit/view/97947742-9941-4dae-b6e1-6d7a47a8c28f

***$K_{1,1}$*(Ca^{2+}/*β*-GlcA):** 0.25 M^{-1}; *Error: ± 1.06 %*
http://app.supramolecular.org/bindfit/view/2c8e3d3c-cbfb-4ada-bf8b-13096825da12

***$K_{1,1}$*(Ca^{2+}/α-GulA):** 2.20 M^{-1}; *Error: ± 2.35 %*
http://app.supramolecular.org/bindfit/view/525ed927-9f35-40ed-9484-f80544b795fe

***$K_{1,1}$*(Ca^{2+}/*β*-GulA):** 0.61 M^{-1}; *Error: ± 1.97 %*
http://app.supramolecular.org/bindfit/view/7a6b7ac3-fb80-42a3-8f7b-d4fc2667fb28

***$K_{1,1}$*(Ca^{2+}/α-ManA):** 0.30 M^{-1}; *Error: ± 1.40 %*
http://app.supramolecular.org/bindfit/view/a7304828-355c-483f-9d74-ceff192ee032

***$K_{1,1}$*(Ca^{2+}/*β*-ManA):** 0.26 M^{-1}; *Error: ± 1.47 %*
http://app.supramolecular.org/bindfit/view/1fb3318b-b575-4799-b351-21c61db8cf1d

Results from fitting the chemical shift data for carbons C1, C5, and C6 are not shown as they were found to have large errors (>~10%), and often did not fit well to a 1:1 assumption. Despite the poor fit, it is interesting to note that the C6 data typically gave rise to $K_{1,1}$ values that were much higher than those calculated from the C2-C4 data above. This finding is consistent with the idea that the carboxylate binding-modes are typically stronger than the hydroxyl-only binding modes at pH 7. However, more granular data and more careful control of the ionic strength of the solution are recommended for a more quantitative evaluation of this effect in future.

Data from the ^{1}H NMR spectroscopic titrations were also fitted using *Bindfit* in a similar manner to the ^{13}C NMR spectral data. However, the much smaller chemical shift changes for the proton data lead to larger errors in the data and the fits were generally of a poorer quality. The ^{13}C fittings reported above were therefore deemed to be more reliable.

3 Supplementary data

3.1 Calcium-uronate binding in the presence of different counter anions

All of the experiments described in the manuscript were conducted with the addition of metal chloride salts as the source of metal ions. In order to verify that the metal-uronate binding interactions described in the paper were not unique to chloride solutions, additional experiments were conducted using calcium iodide and nitrate salts as alternatives (see Figure S.1 below). Aside from the change in anion, the experiments were otherwise identical to those shown in Figure 3 of the main manuscript. The results in Figure S.1 show that the effects of Ca^{2+} on the uronate α/β ratios relative to the metal-free case, were broadly replicated when I^- and NO_3^- were used in place of Cl^-. Patterns of changes to chemical shifts were also largely unchanged in going from Cl^- to I^- to NO_3^- (see Tables in Section 3.3)

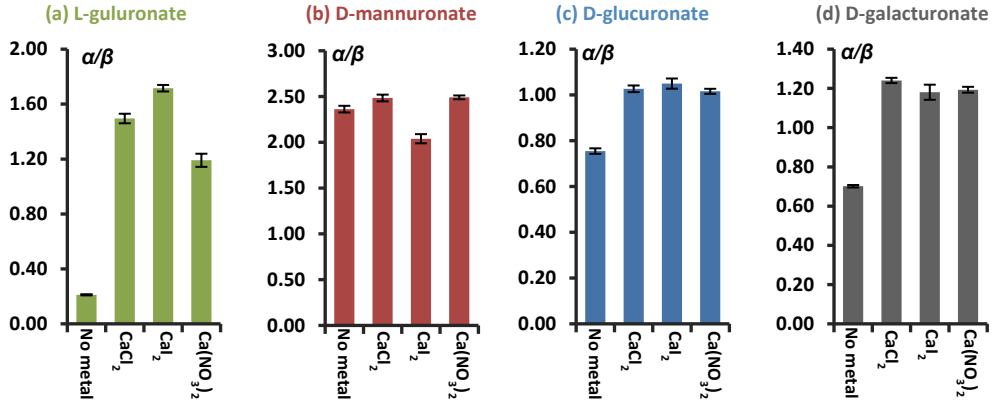

Figure S.1 The α/β ratio of four sodium mono-uronates recorded in 1.0 M solutions of different calcium salts at 295 K and pD 7.9.

3.2 Calcium-uronate binding at different ionic strengths

The role of the ionic strength (*I*) was not explored extensively in this work as it has already been well documented that diluting a metal-saccharide solution decreases the degree of complexation.[12] In the experiments shown in Figure 3 of the main manuscript, a constant [metal]:[uronate] ratio (1:23) was used, meaning that the ionic strength of the solutions containing divalent cations (*I* = 6.09 M) were higher than those of the monovalent cations (*I* = 2.09 M). An experiment was also conducted whereby the Ca^{2+} concentration was reduced from 1.0 M to 0.2 M (giving a lower [metal]:[uronate] ratio of 1:4.6) to give a solution of much lower ionic strength (*I* = 1.29 M). As anticipated, where there had previously been changes to the α/β ratio on inclusion of Ca^{2+} (1.0 M), such differences were much smaller at the lower concentration (0.2 M) (see Figure S.2). In the case of **GulA** and **GalA**, however, the influence Ca^{2+} ions at the lower concentration (0.2 M) was still much larger than the impact of including monovalent cations (such as Na^{+}) at a higher concentration (1.0 M).

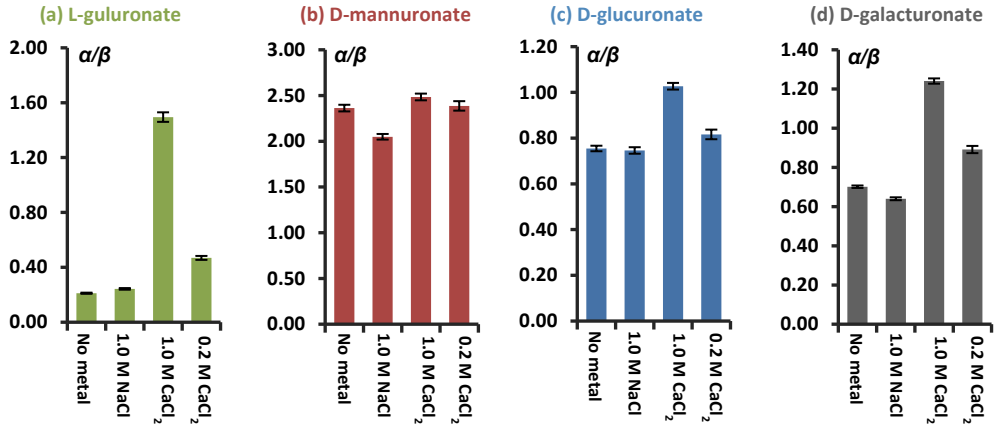

Figure S.2 The α/β ratio of four sodium mono-uronates recorded in different concentration solutions of metal salts at 295 K and pD 7.9.

3.3 Tables of Δδ values for metal-uronate solutions

Table S.4 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-L-guluronate (**GulA**) in metal chloride salts at pD 7.9

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	7.9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	7.9	-0.03	-0.04	-0.04	-0.07	-0.04	-0.05	-0.05	-0.04	-0.06	-0.05
1.0 M KCl	7.9	-0.05	-0.06	-0.05	-0.08	-0.06	-0.06	-0.06	-0.06	-0.07	-0.06
1.0 M $CaCl_2$	7.9	0.17	0.09	0.02	-0.10	0.10	-0.02	-0.03	-0.07	-0.08	-0.01
1.0 M $SrCl_2$	7.9	0.12	0.04	-0.02	-0.16	0.05	-0.05	-0.06	-0.09	-0.12	-0.04
1.0 M $BaCl_2$	7.9	0.07	-0.01	-0.07	-0.20	0.02	-0.03	-0.08	-0.12	-0.16	-0.04
1.0 M $MgCl_2$	7.9	-0.02	-0.08	-0.07	-0.09	-0.04	-0.09	-0.09	-0.09	-0.10	-0.08
1.0 M $Ca(NO_3)_2$	7.9	0.22	0.13	0.08	-0.01	0.17	0.05	0.04	0.02	0.00	0.06
1.0 M CaI_2	7.9	0.08	0.00	-0.05	-0.21	0.00	-0.09	-0.12	-0.14	-0.18	-0.08
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	7.9	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	7.9	0.04	0.03	0.04	-	0.04	0.01	0.01	0.02	-	0.02
1.0 M KCl	7.9	0.03	0.02	0.03	-	0.01	0.01	0.01	0.01	-	0.01
1.0 M $CaCl_2$	7.9	0.27	0.19	0.13	-	0.20	0.05	0.04	0.01	-	0.07
1.0 M $SrCl_2$	7.9	0.28	0.20	0.14	-	0.22	0.07	0.06	0.03	-	0.08
1.0 M $BaCl_2$	7.9	0.28	0.20	0.14	-	0.22	0.12	0.07	0.03	-	0.11
1.0 M $MgCl_2$	7.9	0.06	0.00	0.02	-	0.04	0.01	0.00	0.01	-	0.02
1.0 M $Ca(NO_3)_2$	7.9	0.24	0.15	0.09	-	0.19	0.05	0.04	0.02	-	0.06
1.0 M CaI_2	7.9	0.28	0.21	0.15	-	0.21	0.09	0.06	0.05	-	0.10

Table S.5 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-L-guluronate (**GulA**) in metal chloride salts at pD 1.4

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	1.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	1.4	-0.04	-0.04	-0.04	-0.06	-0.04	-0.05	-0.05	-0.04	-0.05	-0.04
1.0 M KCl	1.4	-0.05	-0.06	-0.06	-0.07	-0.06	-0.06	-0.06	-0.06	-0.06	-0.05
1.0 M $CaCl_2$	1.4	0.01	0.04	-0.01	-0.12	0.00	-0.09	-0.09	-0.08	-0.10	-0.09
1.0 M $SrCl_2$	1.4	-0.02	0.00	-0.06	-0.16	-0.03	-0.11	-0.12	-0.10	-0.12	-0.11
1.0 M $BaCl_2$	1.4	-0.04	-0.05	-0.10	-0.19	-0.06	-0.10	-0.13	-0.14	-0.15	-0.11
1.0 M $MgCl_2$	1.4	-0.10	-0.10	-0.09	-0.10	-0.12	-0.10	-0.10	-0.10	-0.10	-0.10
1.0 M $ZnCl_2$	1.4	-0.10	-0.11	-0.11	-0.12	-0.15	-0.12	-0.13	-0.12	-0.12	-0.13
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	1.4	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	1.4	0.02	0.02	0.02	-	0.02	0.00	-0.01	0.00	-	0.01
1.0 M KCl	1.4	0.02	0.01	0.01	-	0.01	0.00	0.00	0.00	-	0.01
1.0 M $CaCl_2$	1.4	0.13	0.15	0.10	-	0.11	0.01	0.00	0.02	-	0.01
1.0 M $SrCl_2$	1.4	0.14	0.16	0.10	-	0.12	0.01	0.00	0.02	-	0.01
1.0 M $BaCl_2$	1.4	0.15	0.15	0.10	-	0.14	0.04	0.01	0.01	-	0.04
1.0 M $MgCl_2$	1.4	0.00	0.00	0.01	-	-0.02	-0.01	-0.01	-0.01	-	0.00
1.0 M $ZnCl_2$	1.4	0.02	0.01	0.01	-	-0.03	0.00	0.00	0.00	-	-0.01

Table S.6 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-mannuronate (**ManA**) in metal chloride salts at pD 7.9

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**7.9**	-0.05	-0.04	-0.05	-0.07	-0.05	-0.03	-0.03	-0.02	-0.06	-0.04
1.0 M KCl	**7.9**	-0.06	-0.05	-0.06	-0.08	-0.07	-0.04	-0.05	-0.05	-0.08	-0.06
1.0 M $CaCl_2$	**7.9**	0.03	-0.03	-0.06	-0.11	0.01	0.01	-0.03	-0.02	-0.06	-0.01
1.0 M $SrCl_2$	**7.9**	-0.02	-0.08	-0.10	-0.15	-0.05	-0.03	-0.07	-0.06	-0.10	-0.05
1.0 M $BaCl_2$	**7.9**	-0.06	-0.11	-0.13	-0.16	-0.09	-0.02	-0.08	-0.08	-0.11	-0.07
1.0 M $MgCl_2$	**7.9**	-0.07	-0.06	-0.08	-0.10	-0.06	-0.06	-0.07	-0.05	-0.11	-0.03
1.0 M $Ca(NO_3)_2$	**7.9**	0.09	0.03	0.01	-0.03	0.08	0.04	0.03	0.03	0.00	0.03
1.0 M CaI_2	**7.9**	-0.02	-0.09	-0.14	-0.19	-0.06	0.01	-0.08	-0.03	-0.17	0.00
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**7.9**	0.02	0.03	0.02	-	0.02	0.04	0.03	0.04	-	0.03
1.0 M KCl	**7.9**	0.02	0.03	0.02	-	0.01	0.04	0.03	0.02	-	0.02
1.0 M $CaCl_2$	**7.9**	0.14	0.08	0.05	-	0.12	0.08	0.04	0.04	-	0.05
1.0 M $SrCl_2$	**7.9**	0.12	0.07	0.04	-	0.10	0.08	0.04	0.05	-	0.06
1.0 M $BaCl_2$	**7.9**	0.10	0.05	0.03	-	0.07	0.10	0.03	0.04	-	0.04
1.0 M $MgCl_2$	**7.9**	0.04	0.04	0.03	-	0.04	0.05	0.04	0.05	-	0.07
1.0 M $Ca(NO_3)_2$	**7.9**	0.12	0.06	0.04	-	0.10	0.04	0.03	0.03	-	0.04
1.0 M CaI_2	**7.9**	0.17	0.10	0.05	-	0.14	0.18	0.09	0.14	-	0.17

Table S.7 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-mannuronate (**ManA**) in metal chloride salts at pD 1.4

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**1.4**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**1.4**	-0.04	-0.04	-0.04	-0.05	-0.04	-0.02	-0.03	-0.02	-0.06	-0.02
1.0 M KCl	**1.4**	-0.06	-0.06	-0.07	-0.06	-0.06	-0.04	-0.05	-0.04	-0.08	-0.02
1.0 M $CaCl_2$	**1.4**	-0.08	-0.08	-0.10	-0.09	-0.09	-0.04	-0.06	-0.04	-0.10	-0.05
1.0 M $SrCl_2$	**1.4**	-0.11	-0.11	-0.13	-0.13	-0.12	-0.07	-0.09	-0.08	-0.13	-0.07
1.0 M $BaCl_2$	**1.4**	-0.13	-0.14	-0.16	-0.16	-0.13	-0.07	-0.11	-0.10	-0.15	-0.06
1.0 M $MgCl_2$	**1.4**	-0.09	-0.08	-0.10	-0.10	-0.09	-0.06	-0.07	-0.06	-0.11	-0.06
1.0 M $ZnCl_2$	**1.4**	-0.08	-0.09	-0.10	-0.13	-0.13	-0.07	-0.09	-0.07	-0.13	-0.10
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**1.4**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**1.4**	0.01	0.01	0.01	-	0.01	0.04	0.03	0.03	-	0.04
1.0 M KCl	**1.4**	0.00	0.00	-0.01	-	0.00	0.04	0.03	0.04	-	0.05
1.0 M $CaCl_2$	**1.4**	0.01	0.02	0.00	-	0.01	0.05	0.04	0.05	-	0.05
1.0 M $SrCl_2$	**1.4**	0.02	0.02	0.00	-	0.02	0.06	0.04	0.05	-	0.06
1.0 M $BaCl_2$	**1.4**	0.03	0.02	0.00	-	0.02	0.08	0.04	0.04	-	0.08
1.0 M $MgCl_2$	**1.4**	0.01	0.02	0.00	-	0.01	0.05	0.04	0.06	-	0.05
1.0 M $ZnCl_2$	**1.4**	0.05	0.04	0.03	-	0.00	0.06	0.04	0.06	-	0.04

Table S.8 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-glucuronate (**GlcA**) in metal chloride salts at pD 7.9

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**7.9**	-0.04	-0.05	-0.06	-0.06	-0.06	-0.04	-0.05	-0.05	-0.05	-0.04
1.0 M KCl	**7.9**	-0.06	-0.06	-0.07	-0.07	-0.06	-0.05	-0.07	-0.06	-0.06	-0.05
1.0 M $CaCl_2$	**7.9**	0.00	-0.06	-0.08	-0.07	-0.03	-0.06	-0.08	-0.08	-0.08	-0.03
1.0 M $SrCl_2$	**7.9**	-0.04	-0.09	-0.12	-0.11	-0.08	-0.09	-0.11	-0.11	-0.11	-0.07
1.0 M $BaCl_2$	**7.9**	-0.08	-0.12	-0.14	-0.13	-0.12	-0.09	-0.12	-0.13	-0.13	-0.08
1.0 M $MgCl_2$	**7.9**	-0.07	-0.08	-0.10	-0.09	-0.07	-0.07	-0.09	-0.08	-0.09	-0.05
1.0 M $Ca(NO_3)_2$	**7.9**	0.07	0.00	0.00	0.00	0.05	0.00	-0.01	0.00	0.00	0.03
1.0 M CaI_2	**7.9**	-0.06	-0.12	-0.15	-0.13	-0.10	-0.06	-0.14	-0.09	-0.14	-0.04
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**7.9**	0.02	0.02	0.01	-	0.01	0.02	0.00	0.00	-	0.02
1.0 M KCl	**7.9**	0.01	0.01	-0.01	-	0.00	0.01	0.00	0.00	-	0.01
1.0 M $CaCl_2$	**7.9**	0.08	0.02	-0.01	-	0.05	0.03	0.00	0.00	-	0.05
1.0 M $SrCl_2$	**7.9**	0.06	0.02	-0.01	-	0.03	0.02	0.00	0.00	-	0.04
1.0 M $BaCl_2$	**7.9**	0.05	0.01	-0.01	-	0.01	0.03	0.01	0.00	-	0.05
1.0 M $MgCl_2$	**7.9**	0.02	0.00	-0.01	-	0.01	0.02	-0.01	0.01	-	0.04
1.0 M $Ca(NO_3)_2$	**7.9**	0.07	0.00	0.00	-	0.06	0.00	-0.01	0.00	-	0.03
1.0 M CaI_2	**7.9**	0.03	0.01	-0.01	-	0.01	0.04	0.00	0.02	-	0.05

Table S.9 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-glucuronate (**GlcA**) in metal chloride salts at pD 1.4

Solution	pD	alpha pyranose					beta pyranose				
		Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**1.4**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**1.4**	-0.04	-0.05	-0.05	-0.05	-0.05	-0.04	-0.05	-0.04	-0.05	-0.03
1.0 M KCl	**1.4**	-0.05	-0.06	-0.07	-0.06	-0.06	-0.05	-0.06	-0.05	-0.06	-0.04
1.0 M $CaCl_2$	**1.4**	-0.08	-0.08	-0.10	-0.09	-0.11	-0.08	-0.09	-0.08	-0.10	-0.08
1.0 M $SrCl_2$	**1.4**	-0.11	-0.11	-0.13	-0.12	-0.14	-0.11	-0.12	-0.11	-0.13	-0.11
1.0 M $BaCl_2$	**1.4**	-0.13	-0.13	-0.15	-0.14	-0.16	-0.13	-0.14	-0.13	-0.15	-0.12
1.0 M $MgCl_2$	**1.4**	-0.08	-0.08	-0.10	-0.08	-0.11	-0.07	-0.09	-0.07	-0.10	-0.07
1.0 M $ZnCl_2$	**1.4**	-0.08	-0.09	-0.11	-0.10	-0.13	-0.08	-0.10	-0.09	-0.11	-0.10
		Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)									
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**1.4**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**1.4**	0.01	0.00	-0.01	-	0.00	0.02	0.01	0.02	-	0.02
1.0 M KCl	**1.4**	0.01	0.00	-0.01	-	0.00	0.02	0.00	0.01	-	0.02
1.0 M $CaCl_2$	**1.4**	0.01	0.01	-0.01	-	-0.02	0.02	0.01	0.03	-	0.03
1.0 M $SrCl_2$	**1.4**	0.01	0.00	-0.01	-	-0.02	0.02	0.01	0.03	-	0.03
1.0 M $BaCl_2$	**1.4**	0.01	0.00	-0.01	-	-0.02	0.02	0.01	0.02	-	0.03
1.0 M $MgCl_2$	**1.4**	0.00	0.00	-0.01	-	-0.02	0.03	0.01	0.03	-	0.03
1.0 M $ZnCl_2$	**1.4**	0.02	0.01	-0.01	-	-0.03	0.03	0.01	0.03	-	0.01

Table S.10 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-galacturonate (**GalA**) in metal chloride salts at pD 7.9

Solution	pD	alpha pyranose					beta pyranose				
Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)											
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**7.9**	-0.04	-0.06	-0.05	-0.06	-0.04	-0.02	-0.06	-0.03	-0.06	-0.03
1.0 M KCl	**7.9**	-0.04	-0.06	-0.06	-0.07	-0.05	-0.03	-0.07	-0.04	-0.07	-0.03
1.0 M $CaCl_2$	**7.9**	0.11	-0.05	-0.05	-0.07	0.06	0.02	-0.05	-0.03	-0.07	0.05
1.0 M $SrCl_2$	**7.9**	0.05	-0.10	-0.10	-0.12	0.00	-0.01	-0.08	-0.07	-0.13	0.00
1.0 M $BaCl_2$	**7.9**	0.01	-0.12	-0.13	-0.16	-0.04	0.00	-0.10	-0.10	-0.16	0.00
1.0 M $MgCl_2$	**7.9**	-0.01	-0.09	-0.07	-0.08	-0.01	-0.05	-0.10	-0.05	-0.09	-0.03
1.0 M $Ca(NO_3)_2$	**7.9**	0.15	0.00	0.01	0.00	0.12	0.05	0.01	0.01	-0.01	0.07
1.0 M CaI_2	**7.9**	0.02	-0.15	-0.13	-0.16	-0.02	0.01	-0.12	-0.06	-0.12	-0.01
Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)											
		αH1	**αH2**	**αH3**	**αH4**	**αH5**	**βH1**	**βH2**	**βH3**	**βH4**	**βH5**
No metal	**7.9**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**7.9**	0.03	0.01	0.01	-	0.02	0.04	0.00	0.03	-	0.04
1.0 M KCl	**7.9**	0.02	0.01	0.01	-	0.02	0.04	0.00	0.03	-	0.03
1.0 M $CaCl_2$	**7.9**	0.18	0.01	0.02	-	0.13	0.09	0.02	0.04	-	0.12
1.0 M $SrCl_2$	**7.9**	0.17	0.02	0.03	-	0.12	0.11	0.04	0.05	-	0.13
1.0 M $BaCl_2$	**7.9**	0.17	0.04	0.03	-	0.12	0.16	0.06	0.06	-	0.16
1.0 M $MgCl_2$	**7.9**	0.07	-0.01	0.01	-	0.07	0.03	-0.02	0.03	-	0.05
1.0 M $Ca(NO_3)_2$	**7.9**	0.15	0.00	0.01	-	0.12	0.05	0.02	0.01	-	0.07
1.0 M CaI_2	**7.9**	0.18	0.01	0.03	-	0.14	0.17	0.04	0.10	-	0.15

Table S.11 $\Delta\delta_{obs}$ and $\Delta\delta_{rel}$ values for Na-D-galacturonate (**GalA**) in metal chloride salts at pD 1.4

Solution	pD	alpha pyranose					beta pyranose				
Absolute change in chemical shift compared to metal-free solution ($\Delta\delta_{obs}$)											
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	**1.4**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.0 M NaCl	**1.4**	-0.04	-0.06	-0.05	-0.05	-0.04	-0.03	-0.06	-0.03	-0.05	-0.02
1.0 M KCl	**1.4**	-0.04	-0.06	-0.05	-0.06	-0.05	-0.03	-0.07	-0.03	-0.05	-0.02
1.0 M $CaCl_2$	**1.4**	-0.04	-0.08	-0.07	-0.08	-0.08	-0.05	-0.09	-0.05	-0.08	-0.05
1.0 M $SrCl_2$	**1.4**	-0.07	-0.12	-0.11	-0.12	-0.10	-0.08	-0.13	-0.09	-0.12	-0.08
1.0 M $BaCl_2$	**1.4**	-0.08	-0.15	-0.13	-0.15	-0.12	-0.07	-0.14	-0.11	-0.15	-0.09
1.0 M $MgCl_2$	**1.4**	-0.08	-0.10	-0.09	-0.09	-0.09	-0.06	-0.11	-0.06	-0.09	-0.06
1.0 M $ZnCl_2$	**1.4**	-0.07	-0.12	-0.11	-0.12	-0.15	-0.08	-0.13	-0.08	-0.12	-0.10
Change in chemical shift compared to metal-free solution relative to H4 ($\Delta\delta_{rel}$)											
		αH1	αH2	αH3	αH4	αH5	βH1	βH2	βH3	βH4	βH5
No metal	**1.4**	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	-	0.00
1.0 M NaCl	**1.4**	0.01	-0.01	0.00	-	0.01	0.02	-0.01	0.02	-	0.03
1.0 M KCl	**1.4**	0.01	0.00	0.00	-	0.01	0.03	-0.01	0.02	-	0.03
1.0 M $CaCl_2$	**1.4**	0.04	0.00	0.01	-	0.00	0.03	-0.01	0.03	-	0.03
1.0 M $SrCl_2$	**1.4**	0.05	0.00	0.01	-	0.02	0.04	-0.01	0.03	-	0.04
1.0 M $BaCl_2$	**1.4**	0.07	0.00	0.02	-	0.03	0.07	0.01	0.04	-	0.06
1.0 M $MgCl_2$	**1.4**	0.01	-0.01	0.00	-	0.00	0.03	-0.02	0.03	-	0.03
1.0 M $ZnCl_2$	**1.4**	0.05	0.00	0.01	-	-0.03	0.04	-0.01	0.04	-	0.02

3.4 Tables of equilibrium populations for metal-uronate solutions

Table S.12 Equilibrium populations of isomers of L-guluronate (**GulA**) under various conditions (295 K)

L-guluronate (GulA)									
Solution	**pD**	**%αP**	**±σ**	**%βP**	**±σ**	**%F**	**±σ**	**α/β**	**±σ**
No metal	7.9	**16.6**	*0.3*	**78.6**	*0.4*	**4.8**	*0.9*	**0.21**	*0.00*
1.0 M NaCl	7.9	**18.9**	*0.5*	**77.6**	*0.2*	**3.6**	*0.4*	**0.24**	*0.01*
1.0 M KCl	7.9	**15.6**	*0.4*	**80.7**	*0.2*	**3.7**	*0.5*	**0.19**	*0.01*
1.0 M $MgCl_2$	7.9	**19.6**	*0.4*	**74.4**	*0.5*	**6.0**	*0.5*	**0.26**	*0.01*
1.0 M $SrCl_2$	7.9	**51.3**	*0.4*	**42.6**	*0.7*	**6.2**	*0.3*	**1.20**	*0.02*
1.0 M $BaCl_2$	7.9	**35.1**	*0.1*	**60.8**	*0.5*	**4.1**	*0.1*	**0.58**	*0.00*
1.0 M $CaCl_2$	7.9	**54.7**	*0.8*	**36.6**	*0.7*	**9.0**	*0.3*	**1.50**	*0.03*
1.0 M CaI_2	7.9	**56.2**	*0.3*	**32.7**	*0.4*	**11.1**	*0.4*	**1.72**	*0.02*
1.0 M $Ca(NO_3)_2$	7.9	**48.5**	*1.3*	**40.7**	*1.2*	**10.8**	*0.1*	**1.19**	*0.05*
No metal	1.4	**16.7**	*0.2*	**79.0**	*0.2*	**4.2**	*0.4*	**0.21**	*0.00*
1.0 M NaCl	1.4	**19.0**	*0.3*	**77.5**	*0.5*	**3.5**	*0.2*	**0.25**	*0.00*
1.0 M KCl	1.4	**16.1**	*0.3*	**81.0**	*0.4*	**3.0**	*0.3*	**0.20**	*0.00*
1.0 M $MgCl_2$	1.4	**16.7**	*0.3*	**77.6**	*0.4*	**5.7**	*0.1*	**0.21**	*0.00*
1.0 M $SrCl_2$	1.4	**49.0**	*0.4*	**46.4**	*0.3*	**4.6**	*0.7*	**1.05**	*0.01*
1.0 M $BaCl_2$	1.4	**39.2**	*0.2*	**57.4**	*0.7*	**3.4**	*1.1*	**0.68**	*0.01*
1.0 M $CaCl_2$	1.4	**50.4**	*0.4*	**45.4**	*0.7*	**4.3**	*0.6*	**1.11**	*0.02*
1.0 M $ZnCl_2$	1.4	**17.8**	*0.8*	**76.8**	*0.4*	**5.4**	*0.5*	**0.23**	*0.01*

Table S.13 Equilibrium populations of isomers of D-mannuronate (**ManA**) under various conditions (295 K)

D-mannuronate (ManA)									
Solution	**pD**	**%αP**	**±σ**	**%βP**	**±σ**	**%F**	**±σ**	**α/β**	**±σ**
No metal	7.9	**67.1**	*0.8*	**28.4**	*0.3*	**4.7**	*0.5*	**2.36**	*0.04*
1.0 M NaCl	7.9	**63.7**	*0.6*	**31.1**	*0.4*	**5.3**	*1.2*	**2.05**	*0.03*
1.0 M KCl	7.9	**61.6**	*0.3*	**34.7**	*0.3*	**3.7**	*0.2*	**1.77**	*0.02*
1.0 M $MgCl_2$	7.9	**64.8**	*0.7*	**28.2**	*0.1*	**6.7**	*0.4*	**2.29**	*0.03*
1.0 M $SrCl_2$	7.9	**61.8**	*0.5*	**29.5**	*0.1*	**8.6**	*1.1*	**2.10**	*0.02*
1.0 M $BaCl_2$	7.9	**54.7**	*0.6*	**40.2**	*0.4*	**5.2**	*0.2*	**1.36**	*0.02*
1.0 M $CaCl_2$	7.9	**63.1**	*0.6*	**25.4**	*0.3*	**11.4**	*0.3*	**2.48**	*0.04*
1.0 M CaI_2	7.9	**58.9**	*0.7*	**28.9**	*0.6*	**12.2**	*0.4*	**2.04**	*0.05*
1.0 M $Ca(NO_3)_2$	7.9	**61.4**	*0.5*	**24.6**	*0.1*	**14.0**	*0.5*	**2.49**	*0.02*
No metal	1.4	**72.3**	*0.9*	**23.6**	*0.4*	**4.1**	*0.9*	**3.06**	*0.07*
1.0 M NaCl	1.4	**67.6**	*0.5*	**26.8**	*0.4*	**5.7**	*0.4*	**2.52**	*0.05*
1.0 M KCl	1.4	**65.1**	*1.5*	**29.5**	*0.1*	**5.4**	*0.1*	**2.21**	*0.05*
1.0 M $MgCl_2$	1.4	**67.7**	*0.5*	**27.4**	*0.5*	**4.6**	*0.4*	**2.47**	*0.05*
1.0 M $SrCl_2$	1.4	**62.9**	*0.9*	**27.2**	*0.4*	**9.8**	*0.2*	**2.31**	*0.05*
1.0 M $BaCl_2$	1.4	**60.2**	*1.0*	**31.8**	*0.3*	**8.1**	*0.4*	**1.90**	*0.04*
1.0 M $CaCl_2$	1.4	**64.3**	*1.0*	**25.7**	*0.3*	**10.0**	*0.5*	**2.50**	*0.05*
1.0 M $ZnCl_2$	1.4	**68.3**	*0.8*	**25.9**	*0.4*	**5.8**	*0.5*	**2.64**	*0.05*

Table S.14 Equilibrium populations of isomers of D-glucuronate (**GlcA**) under various conditions (295 K)

D-glucuronate (GlcA)									
Solution	**pD**	**%αP**	**±σ**	**%βP**	**±σ**	**%F**	**±σ**	**α/β**	**±σ**
No metal	7.9	**42.4**	*0.7*	**56.2**	*0.2*	**1.4**	*0.1*	**0.75**	*0.01*
1.0 M NaCl	7.9	**42.2**	*0.7*	**56.6**	*0.6*	**1.2**	*0.1*	**0.75**	*0.01*
1.0 M KCl	7.9	**40.0**	*0.8*	**58.3**	*0.5*	**1.7**	*0.3*	**0.69**	*0.01*
1.0 M $MgCl_2$	7.9	**43.4**	*0.9*	**52.8**	*0.3*	**3.7**	*0.3*	**0.82**	*0.02*
1.0 M $SrCl_2$	7.9	**46.9**	*0.6*	**48.3**	*0.1*	**4.8**	*0.2*	**0.97**	*0.01*
1.0 M $BaCl_2$	7.9	**41.5**	*0.4*	**55.2**	*0.7*	**3.3**	*0.3*	**0.75**	*0.01*
1.0 M $CaCl_2$	7.9	**47.0**	*0.6*	**45.8**	*0.3*	**7.1**	*0.0*	**1.03**	*0.01*
1.0 M CaI_2	7.9	**46.9**	*0.8*	**44.7**	*0.5*	**8.4**	*0.1*	**1.05**	*0.02*
1.0 M $Ca(NO_3)_2$	7.9	**47.2**	*0.5*	**46.5**	*0.2*	**6.2**	*0.4*	**1.02**	*0.01*
No metal	1.4	**47.2**	*0.6*	**49.9**	*0.2*	**2.9**	*0.2*	**0.95**	*0.01*
1.0 M NaCl	1.4	**47.0**	*0.6*	**49.9**	*0.2*	**3.1**	*0.2*	**0.94**	*0.01*
1.0 M KCl	1.4	**45.6**	*0.6*	**51.5**	*0.2*	**2.8**	*0.4*	**0.89**	*0.01*
1.0 M $MgCl_2$	1.4	**48.0**	*0.6*	**48.6**	*0.3*	**3.4**	*0.3*	**0.99**	*0.01*
1.0 M $SrCl_2$	1.4	**47.9**	*1.0*	**47.6**	*0.6*	**4.4**	*0.1*	**1.01**	*0.02*
1.0 M $BaCl_2$	1.4	**47.8**	*1.0*	**47.2**	*0.7*	**4.8**	*0.4*	**1.01**	*0.03*
1.0 M $CaCl_2$	1.4	**46.5**	*0.6*	**48.6**	*0.2*	**4.8**	*0.5*	**0.96**	*0.01*
1.0 M $ZnCl_2$	1.4	**47.2**	*1.0*	**48.7**	*0.9*	**4.1**	*0.5*	**0.97**	*0.03*

Table S.15 Equilibrium populations of isomers of D-galacturonate (**GalA**) under various conditions (295 K)

D-galacturonate (GalA)									
Solution	**pD**	**%αP**	**±σ**	**%βP**	**±σ**	**%F**	**±σ**	**α/β**	**±σ**
No metal	7.9	**37.5**	*0.2*	**53.5**	*0.4*	**9.1**	*0.2*	**0.70**	*0.01*
1.0 M NaCl	7.9	**36.2**	*0.3*	**56.6**	*0.4*	**7.2**	*0.1*	**0.64**	*0.01*
1.0 M KCl	7.9	**33.3**	*0.3*	**59.7**	*0.6*	**7.1**	*0.2*	**0.56**	*0.01*
1.0 M $MgCl_2$	7.9	**38.1**	*0.4*	**49.5**	*0.7*	**12.4**	*0.0*	**0.77**	*0.01*
1.0 M $SrCl_2$	7.9	**46.6**	*0.4*	**45.6**	*0.4*	**7.8**	*0.4*	**1.02**	*0.01*
1.0 M $BaCl_2$	7.9	**36.0**	*0.2*	**59.0**	*0.5*	**5.0**	*0.3*	**0.61**	*0.01*
1.0 M $CaCl_2$	7.9	**48.9**	*0.2*	**39.4**	*0.4*	**11.7**	*0.3*	**1.24**	*0.01*
1.0 M CaI_2	7.9	**47.7**	*1.0*	**40.4**	*1.0*	**12.0**	*0.9*	**1.18**	*0.04*
1.0 M $Ca(NO_3)_2$	7.9	**48.1**	*0.2*	**40.3**	*0.5*	**11.6**	*0.3*	**1.19**	*0.01*
No metal	1.4	**42.4**	*0.2*	**47.7**	*0.3*	**9.8**	*0.4*	**0.89**	*0.01*
1.0 M NaCl	1.4	**40.8**	*0.3*	**50.7**	*0.7*	**8.5**	*0.2*	**0.80**	*0.01*
1.0 M KCl	1.4	**38.1**	*0.2*	**54.1**	*0.7*	**7.8**	*0.1*	**0.70**	*0.01*
1.0 M $MgCl_2$	1.4	**40.1**	*0.8*	**50.6**	*0.9*	**9.5**	*0.6*	**0.79**	*0.02*
1.0 M $SrCl_2$	1.4	**43.2**	*0.3*	**48.0**	*0.3*	**8.8**	*0.2*	**0.90**	*0.01*
1.0 M $BaCl_2$	1.4	**40.9**	*0.4*	**51.4**	*0.5*	**7.7**	*0.5*	**0.80**	*0.01*
1.0 M $CaCl_2$	1.4	**43.2**	*0.3*	**47.5**	*0.7*	**9.4**	*0.2*	**0.91**	*0.01*
1.0 M $ZnCl_2$	1.4	**42.0**	*0.3*	**48.5**	*1.3*	**9.6**	*0.5*	**0.87**	*0.02*

3.5 Representative spectra for Ca^{2+}/L-guluronate NMR titrations

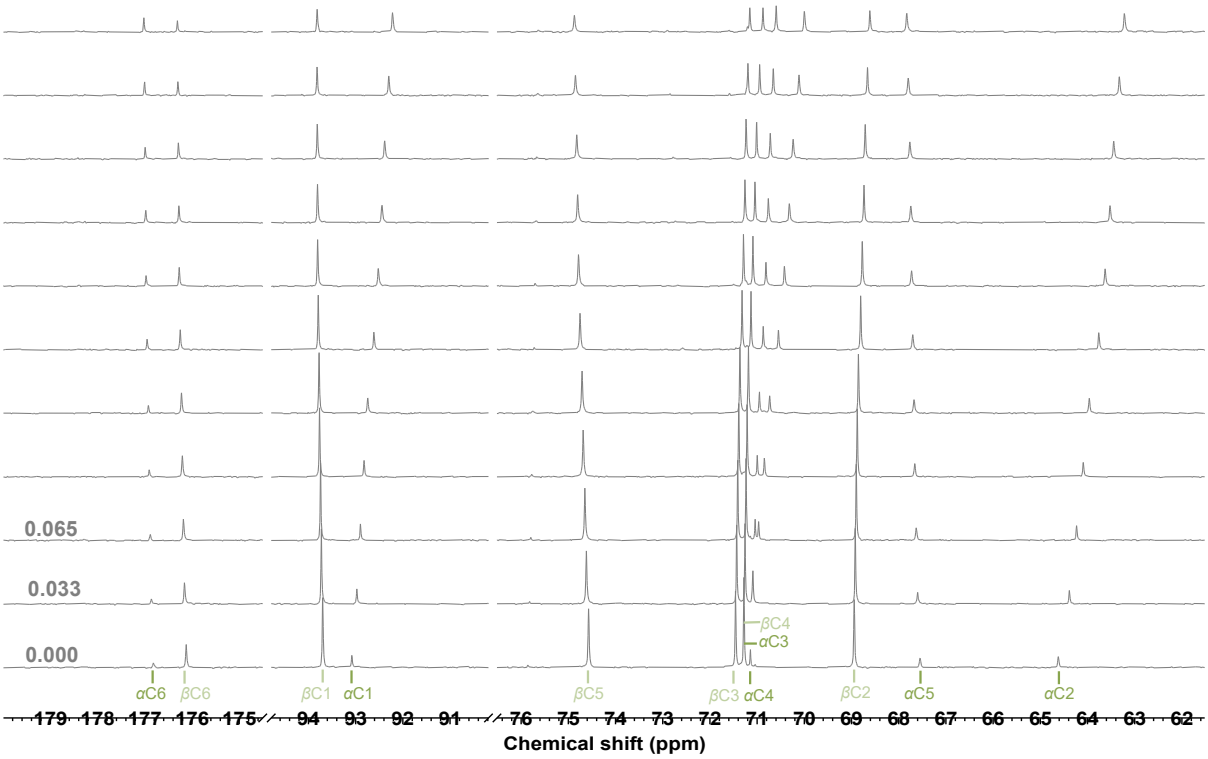

Figure S.3 ^{13}C NMR spectra of sodium L-guluronate (0.26 M) in the presence of different concentrations of $CaCl_2$ (0.00 – 1.30 M). Spectra recorded in D_2O at pD 7.9, 295K, 100 MHz. Signals measured relative to the signal arising from external reference (not shown): $\underline{C}DCl_3$ δ = 77.160 ppm.

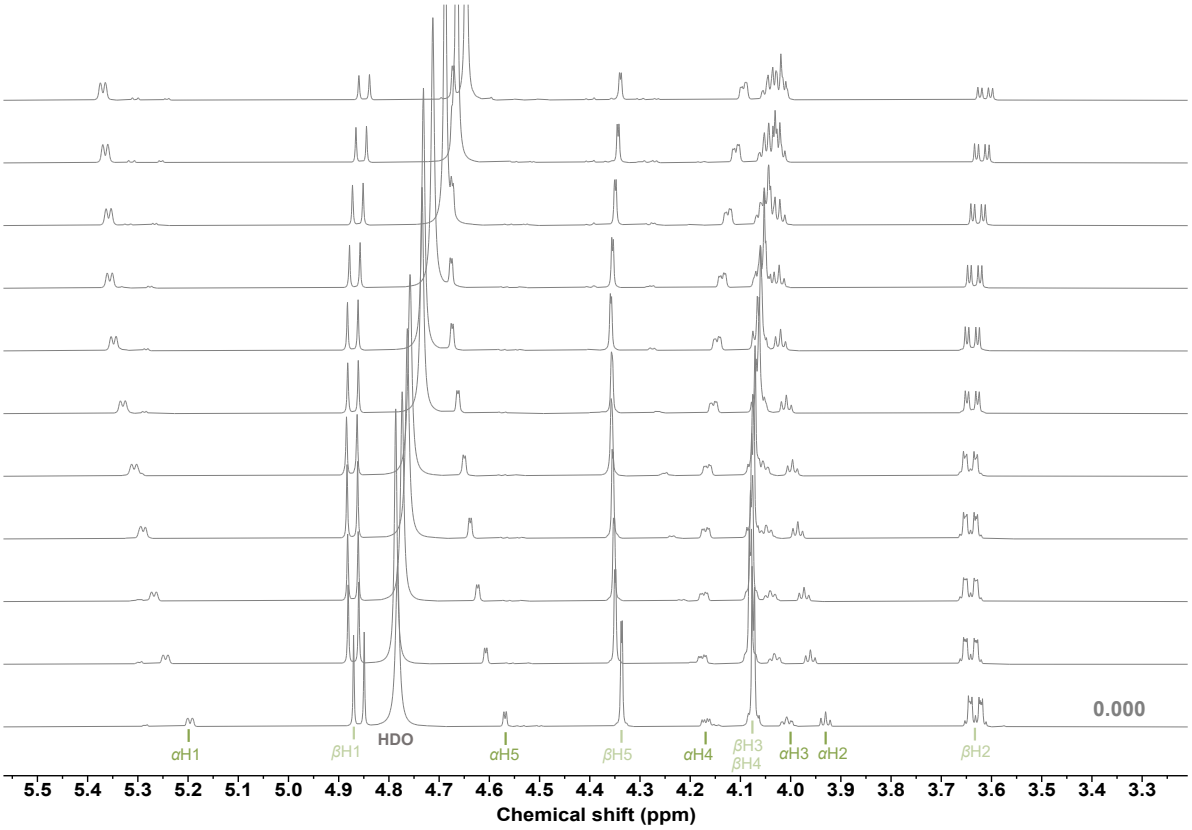

Figure S.4 ^{1}H NMR spectra of sodium L-guluronate (0.26 M) in the presence of different concentrations of $CaCl_2$ (0.00 – 1.30 M). Spectra recorded in D_2O at pD 7.9, 295K, 400 MHz. Signals measured relative to the signal arising from external reference (not shown): $C\underline{H}Cl_3$ in $CDCl_3$ δ = 7.260 ppm.

3.6 Raw data for Ca^{2+}/uronate NMR spectroscopic titrations

3.6.1 Raw data for ^{13}C NMR titrations

	[Ca] / M	[anomer]* / M	Change to ^{13}C NMR chemical shift (ppm) C1	C2	C3	C4	C5	C6
α-L-guluronate (α-GulA)	0.0000	0.0435	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.0475	*-0.070*	*-0.143*	*-0.117*	*-0.033*	*0.026*	*0.020*
	0.0650	0.0530	*-0.114*	*-0.253*	*-0.206*	*-0.059*	*0.053*	*0.047*
	0.1300	0.0588	*-0.204*	*-0.432*	*-0.353*	*-0.115*	*0.080*	*0.069*
	0.1950	0.0688	*-0.283*	*-0.570*	*-0.472*	*-0.162*	*0.113*	*0.090*
	0.2600	0.0769	*-0.358*	*-0.695*	*-0.582*	*-0.206*	*0.129*	*0.109*
	0.3900	0.0881	*-0.483*	*-0.878*	*-0.755*	*-0.281*	*0.157*	*0.133*
	0.5200	0.0996	*-0.574*	*-1.009*	*-0.878*	*-0.337*	*0.181*	*0.158*
	0.6500	0.1106	*-0.649*	*-1.113*	*-0.982*	*-0.389*	*0.197*	*0.168*
	0.7800	0.1130	*-0.706*	*-1.194*	*-1.064*	*-0.429*	*0.217*	*0.179*
	1.0400	0.1340	*-0.796*	*-1.312*	*-1.187*	*-0.496*	*0.254*	*0.189*
	1.3000	0.1503	*-0.870*	*-1.415*	*-1.295*	*-0.553*	*0.285*	*0.206*
β-L-guluronate (β-GulA)	0.0000	0.2165	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.2125	*0.009*	*-0.021*	*-0.018*	*-0.018*	*0.021*	*0.013*
	0.0650	0.2070	*0.026*	*-0.028*	*-0.026*	*-0.027*	*0.049*	*0.037*
	0.1300	0.2012	*0.044*	*-0.058*	*-0.056*	*-0.056*	*0.079*	*0.058*
	0.1950	0.1912	*0.066*	*-0.076*	*-0.076*	*-0.080*	*0.115*	*0.083*
	0.2600	0.1831	*0.074*	*-0.103*	*-0.102*	*-0.106*	*0.140*	*0.100*
	0.3900	0.1719	*0.093*	*-0.145*	*-0.142*	*-0.157*	*0.178*	*0.129*
	0.5200	0.1604	*0.103*	*-0.179*	*-0.172*	*-0.197*	*0.211*	*0.148*
	0.6500	0.1494	*0.106*	*-0.215*	*-0.202*	*-0.239*	*0.229*	*0.159*
	0.7800	0.1470	*0.110*	*-0.244*	*-0.227*	*-0.276*	*0.246*	*0.167*
	1.0400	0.1260	*0.116*	*-0.292*	*-0.267*	*-0.343*	*0.278*	*0.180*
	1.3000	0.1097	*0.118*	*-0.340*	*-0.304*	*-0.410*	*0.302*	*0.190*
α-D-mannuronate (α-ManA)	0.0000	0.1769	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.1781	*0.001*	*-0.009*	*-0.003*	*-0.007*	*-0.032*	*0.006*
	0.0650	0.1793	*0.002*	*-0.009*	*-0.006*	*-0.013*	*-0.041*	*0.014*
	0.1300	0.1806	*0.000*	*-0.029*	*-0.016*	*-0.033*	*-0.084*	*0.027*
	0.1950	0.1793	*-0.008*	*-0.051*	*-0.031*	*-0.059*	*-0.139*	*0.033*
	0.2600	0.1806	*-0.010*	*-0.064*	*-0.038*	*-0.074*	*-0.212*	*0.041*
	0.3900	0.1818	*-0.023*	*-0.102*	*-0.061*	*-0.112*	*-0.353*	*0.047*
	0.5200	0.1806	*-0.034*	*-0.131*	*-0.080*	*-0.145*	*-0.465*	*0.052*
	0.6500	0.1844	*-0.047*	*-0.160*	*-0.093*	*-0.174*	*-0.547*	*0.052*
	0.7800	0.1857	*-0.057*	*-0.188*	*-0.108*	*-0.199*	*-0.629*	*0.046*
	1.0400	0.1857	*-0.081*	*-0.236*	*-0.133*	*-0.247*	*-0.735*	*0.044*
	1.3000	0.1818	*-0.104*	*-0.282*	*-0.156*	*-0.288*	*-0.837*	*0.024*

β-D-mannuronate (β-ManA)								
	0.0000	0.0831	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.0819	*-0.002*	*-0.004*	*-0.011*	*-0.005*	*-0.028*	*0.006*
	0.0650	0.0807	*-0.003*	*-0.004*	*-0.011*	*-0.008*	*-0.020*	*0.008*
	0.1300	0.0794	*-0.013*	*-0.018*	*-0.036*	*-0.023*	*-0.063*	*0.020*
	0.1950	0.0807	*-0.028*	*-0.035*	*-0.055*	*-0.040*	*-0.104*	*0.039*
	0.2600	0.0794	*-0.036*	*-0.044*	*-0.068*	*-0.051*	*-0.158*	*0.042*
	0.3900	0.0782	*-0.066*	*-0.069*	*-0.108*	*-0.080*	*-0.270*	*0.060*
	0.5200	0.0794	*-0.092*	*-0.091*	*-0.137*	*-0.104*	*-0.349*	*0.058*
	0.6500	0.0756	*-0.117*	*-0.112*	*-0.166*	*-0.128*	*-0.415*	*0.058*
	0.7800	0.0743	*-0.139*	*-0.130*	*-0.191*	*-0.148*	*-0.477*	*0.059*
	1.0400	0.0743	*-0.183*	*-0.164*	*-0.234*	*-0.190*	*-0.566*	*0.057*
	1.3000	0.0782	*-0.227*	*-0.199*	*-0.275*	*-0.225*	*-0.646*	*0.056*

α-D-glucuronate (α-GlcA)								
	0.0000	0.1092	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0650	0.1106	*-0.005*	*-0.036*	*-0.007*	*-0.040*	*-0.049*	*0.022*
	0.1300	0.1111	*-0.007*	*-0.063*	*-0.008*	*-0.065*	*-0.096*	*0.036*
	0.1950	0.1121	*-0.012*	*-0.092*	*-0.013*	*-0.091*	*-0.130*	*0.049*
	0.2600	0.1140	*-0.019*	*-0.120*	*-0.017*	*-0.118*	*-0.167*	*0.053*
	0.3900	0.1182	*-0.029*	*-0.163*	*-0.025*	*-0.163*	*-0.233*	*0.058*
	0.5200	0.1204	*-0.041*	*-0.207*	*-0.029*	*-0.203*	*-0.288*	*0.060*
	0.6500	0.1209	*-0.053*	*-0.249*	*-0.039*	*-0.244*	*-0.344*	*0.055*
	0.7800	0.1244	*-0.065*	*-0.287*	*-0.045*	*-0.280*	*-0.393*	*0.051*
	1.0400	0.1281	*-0.091*	*-0.366*	*-0.056*	*-0.352*	*-0.486*	*0.040*
	1.3000	0.1313	*-0.110*	*-0.434*	*-0.064*	*-0.415*	*-0.573*	*0.023*

β-D-glucuronate (β-GlcA)								
	0.0000	0.1508	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0650	0.1494	*-0.013*	*-0.022*	*-0.013*	*-0.022*	*-0.047*	*0.023*
	0.1300	0.1489	*-0.021*	*-0.035*	*-0.020*	*-0.032*	*-0.088*	*0.041*
	0.1950	0.1479	*-0.032*	*-0.052*	*-0.032*	*-0.044*	*-0.120*	*0.058*
	0.2600	0.1460	*-0.045*	*-0.069*	*-0.043*	*-0.058*	*-0.157*	*0.066*
	0.3900	0.1418	*-0.067*	*-0.095*	*-0.058*	*-0.083*	*-0.224*	*0.076*
	0.5200	0.1396	*-0.088*	*-0.120*	*-0.077*	*-0.104*	*-0.282*	*0.087*
	0.6500	0.1391	*-0.113*	*-0.147*	*-0.095*	*-0.127*	*-0.340*	*0.086*
	0.7800	0.1356	*-0.133*	*-0.172*	*-0.107*	*-0.147*	*-0.390*	*0.089*
	1.0400	0.1319	*-0.178*	*-0.225*	*-0.142*	*-0.190*	*-0.493*	*0.088*
	1.3000	0.1287	*-0.212*	*-0.269*	*-0.165*	*-0.227*	*-0.590*	*0.081*

*The nominal total concentration of uronate in solution was 0.26 M. The value "[anomer]" is the actual concentration of the named uronate anomer, calculated at each value of [Ca^{2+}].

3.6.2 Raw data for ^{1}H NMR titrations

	[Ca] / M	[anomer]* / M	Change to ^{1}H NMR chemical shift (ppm) H1	H2	H3	H4	H5
α-L-guluronate (α-GulA)	0.0000	0.0435	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.0475	*0.027*	*0.018*	*0.015*	*0.004*	*0.022*
	0.0650	0.0530	*0.038*	*0.024*	*0.020*	*0.005*	*0.031*
	0.1300	0.0588	*0.059*	*0.035*	*0.028*	*0.002*	*0.045*
	0.1950	0.0688	*0.087*	*0.052*	*0.039*	*0.000*	*0.065*
	0.2600	0.0769	*0.107*	*0.063*	*0.046*	*-0.003*	*0.079*
	0.3900	0.0881	*0.124*	*0.072*	*0.052*	*-0.013*	*0.087*
	0.5200	0.0996	*0.147*	*0.087*	*0.056*	*-0.018*	*0.104*
	0.6500	0.1106	*0.158*	*0.092*	*0.058*	*-0.028*	*0.108*
	0.7800	0.1130	*0.163*	*0.093*	*0.057*	*-0.039*	*0.108*
	1.0400	0.1340	*0.167*	*0.092*	*0.053*	*-0.051*	*0.108*
	1.3000	0.1503	*0.175*	*0.092*	*0.047*	*-0.067*	*0.108*
β-L-guluronate (β-GulA)	0.0000	0.2165	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.2125	*0.007*	*0.005*	*0.000*	*0.000*	*0.006*
	0.0650	0.2070	*0.009*	*0.008*	*0.003*	*0.003*	*0.010*
	0.1300	0.2012	*0.008*	*0.007*	*0.002*	*0.002*	*0.012*
	0.1950	0.1912	*0.011*	*0.010*	*0.000*	*0.000*	*0.016*
	0.2600	0.1831	*0.013*	*0.010*	*-0.002*	*-0.002*	*0.019*
	0.3900	0.1719	*0.010*	*0.006*	*-0.007*	*-0.007*	*0.018*
	0.5200	0.1604	*0.013*	*0.008*	*-0.009*	*-0.013*	*0.022*
	0.6500	0.1494	*0.010*	*0.004*	*-0.014*	*-0.020*	*0.019*
	0.7800	0.1470	*0.005*	*-0.002*	*-0.022*	*-0.027*	*0.015*
	1.0400	0.1260	*-0.002*	*-0.008*	*-0.031*	*-0.037*	*0.010*
	1.3000	0.1097	*-0.006*	*-0.014*	*-0.039*	*-0.050*	*0.007*
α-D-mannuronate (α-ManA)	0.0000	0.1769	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.1781	*0.005*	*0.002*	*0.000*	*-0.001*	*0.005*
	0.0650	0.1793	*0.009*	*0.005*	*0.005*	*0.003*	*0.007*
	0.1300	0.1806	*0.014*	*0.005*	*0.003*	*-0.001*	*0.009*
	0.1950	0.1793	*0.023*	*0.007*	*0.002*	*-0.003*	*0.015*
	0.2600	0.1806	*0.027*	*0.006*	*0.001*	*-0.008*	*0.018*
	0.3900	0.1818	*0.035*	*0.005*	*-0.003*	*-0.016*	*0.022*
	0.5200	0.1806	*0.039*	*0.002*	*-0.010*	*-0.028*	*0.023*
	0.6500	0.1844	*0.043*	*-0.002*	*-0.015*	*-0.038*	*0.023*
	0.7800	0.1857	*0.046*	*-0.005*	*-0.020*	*-0.047*	*0.023*
	1.0400	0.1857	*0.047*	*-0.012*	*-0.031*	*-0.062*	*0.022*
	1.3000	0.1818	*0.048*	*-0.020*	*-0.042*	*-0.080*	*0.021*

β-D-mannuronate (β-ManA)							
	0.0000	0.0831	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0325	0.0819	*0.003*	*0.002*	*0.001*	*0.000*	*0.002*
	0.0650	0.0807	*0.006*	*0.005*	*0.006*	*0.004*	*0.006*
	0.1300	0.0794	*0.008*	*0.005*	*0.005*	*0.002*	*0.008*
	0.1950	0.0807	*0.013*	*0.008*	*0.009*	*0.002*	*0.014*
	0.2600	0.0794	*0.015*	*0.008*	*0.011*	*-0.001*	*0.015*
	0.3900	0.0782	*0.018*	*0.006*	*0.013*	*-0.006*	*0.014*
	0.5200	0.0794	*0.019*	*0.002*	*0.013*	*-0.011*	*0.010*
	0.6500	0.0756	*0.019*	*-0.001*	*0.011*	*-0.019*	*0.005*
	0.7800	0.0743	*0.020*	*-0.003*	*0.006*	*-0.025*	*-0.002*
	1.0400	0.0743	*0.018*	*-0.009*	*0.002*	*-0.035*	*-0.008*
	1.3000	0.0782	*0.016*	*-0.018*	*-0.008*	*-0.043*	*-0.021*

α-D-glucuronate (α-GlcA)							
	0.0000	0.1092	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0650	0.1106	*0.006*	*-0.001*	*-0.003*	*-0.004*	*0.004*
	0.1300	0.1111	*0.010*	*-0.003*	*-0.004*	*-0.006*	*0.006*
	0.1950	0.1121	*0.014*	*-0.004*	*-0.005*	*-0.006*	*0.007*
	0.2600	0.1140	*0.015*	*-0.007*	*-0.009*	*-0.011*	*0.008*
	0.3900	0.1182	*0.015*	*-0.015*	*-0.019*	*-0.021*	*0.002*
	0.5200	0.1204	*0.017*	*-0.020*	*-0.025*	*-0.027*	*0.002*
	0.6500	0.1209	*0.018*	*-0.023*	*-0.031*	*-0.031*	*0.001*
	0.7800	0.1244	*0.017*	*-0.028*	*-0.038*	*-0.038*	*-0.004*
	1.0400	0.1281	*0.021*	*-0.033*	*-0.047*	*-0.043*	*-0.004*
	1.3000	0.1313	*0.019*	*-0.041*	*-0.059*	*-0.057*	*-0.010*

β-D-glucuronate (β-GlcA)							
	0.0000	0.1508	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
	0.0650	0.1494	*-0.001*	*-0.003*	*-0.005*	*-0.003*	*0.003*
	0.1300	0.1489	*-0.002*	*-0.006*	*-0.005*	*-0.004*	*0.002*
	0.1950	0.1479	*-0.003*	*-0.008*	*-0.008*	*-0.008*	*-0.001*
	0.2600	0.1460	*-0.005*	*-0.012*	*-0.012*	*-0.011*	*-0.001*
	0.3900	0.1418	*-0.013*	*-0.022*	*-0.023*	*-0.023*	*-0.003*
	0.5200	0.1396	*-0.017*	*-0.029*	*-0.029*	*-0.029*	*-0.005*
	0.6500	0.1391	*-0.021*	*-0.035*	*-0.034*	*-0.034*	*-0.006*
	0.7800	0.1356	*-0.027*	*-0.043*	*-0.042*	*-0.042*	*-0.009*
	1.0400	0.1319	*-0.030*	*-0.050*	*-0.048*	*-0.048*	*-0.013*
	1.3000	0.1287	*-0.039*	*-0.061*	*-0.055*	*-0.055*	*-0.018*

*The nominal total concentration of uronate in solution was 0.26 M. The value "[anomer]" is the actual concentration of the named uronate anomer, calculated at each value of [Ca^{2+}].

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